SECOND QUARTERLY REPORT

STUDIES OF REACTION GEOMETRY IN OXIDATION AND REDUCTION

OF THE ALKALINE SILVER ELECTRODE

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ABSTRACT

A polarization curve of the silver anode in ammoniacal electrolyte suitable for use in comparing our current density distribution data with a theoretical analysis of current density distribution has been obtained. Attempts to use this system in a determination of surface area of a sintered silver electrode have failed.

Sintered silver electrodes consisting of spherical silver particles of known diameters were prepared. These were oxidized and their effective electrolytic surface area was determined. These experimental surface areas agreed well with calculated areas when particles in the 24-48 micron size range were used. Agreement was not as good with smaller particles.

Silver foil electrodes were oxidized with and without ultrasonic vibrations to determine the effect these vibrations would have on the charging capacity. Increases of 8% and 25% were observed for two different current densities. These increases are attributed to increased surface area caused by fracturing of the oxide layer by the vibrations.

SECTION I

POTENTIAL AND CURRENT VARIATIONS

OVER THE ELECTRODE SURFACE

(POLARIZATION MEASUREMENTS)

Introduction

In the experimental program of determining how temperature, electrolyte conductivity, and average current density affect current density distribution over the surface of silver electrodes, we are attempting to compare our data with the theoretical predictions of Wagner[1]. The results of Wagner's analysis include families of curves showing the ratio of local current density to average current density (J/J_{ave}) as a function of distance across the electrode surface for particular values of the ratio k_a/a. The parameter k_a is equal to the product of the conductivity of the electrolyte, σ, and the slope of the anodic polarization curve, h_a; a is the half-width of the anode. Therefore,

$$k_a/a = \sigma h_a/a = \sigma/a \left| d\Delta E/dJ \right|$$

Before precise comparisons can be made of the distribution of current density with Wagner's theory, experimental values of h_a and σ are needed. Data on conductivity of the electrolyte are readily determined. The determination of the polarization curve of the silver anode in ammoniacal electrolyte is reported here.

Experimental

The modified Haring cell and Luggin capillary measuring system have been described[2,3]. The capillaries used here, however, were different from

those described previously. The capillaries had been made from 3 mm soft glass tubing with an approximately 3 mm long piece of Intramedic polyethylene tubing (O. D. .61 mm, I. D. .28 mm) sealed into a constricted end with epoxy cement. The seal was tested for electrical leakage prior to use. It has been observed that the epoxy seal occasionally developed an electrical leak after the capillary had been in service. This resulted in higher potential measurements because the potential measured was the potential at the leak in the epoxy seal. Thus the IR-drop between the capillary tip and the seal was included in the potential measurement. To avoid this leakage and yet to permit easy comparison with earlier measurements, glass capillaries were selected for use which had tip dimensions close to those of the polyethylene tubing. For example, the inside diameters and outside diameters of the capillaries used for the experiments reported here were:

	I. D.	O. D.
#1	.27 mm	.67 mm
#2	.27 mm	.66 mm

The polyethylene capillary measurements are I. D. .28 mm and O.D. .61 mm.

The electrolyte used for all experiments in this report contained the following species in the concentrations shown.

14.7	$\underline{N}$	NH_4OH
0.10	$\underline{N}$	KNO_3
0.025	$\underline{N}$	$AgNO_3$

All materials used were reagent grade.

Polarization Curve Determination

The method used in obtaining data for this curve is described in an earlier report[3]. Briefly stated, the procedure is to measure the electrode potential for several different current densities. The methods used to reduce concentration overpotential, non-uniform current distribution, capillary shielding, and IR-drop are also discussed in that report. The procedure for eliminating IR-drop from the potential measurements involves the measurement of potential at various known distances from the electrode surface and the extrapolation of these potentials to the potential at the electrode surface. The extrapolation of these data was done by a least squares computer program. A sample of these extrapolated data is in Table 1. The polarization curve for the silver foil anode is shown in Figure 1.

There are still some problems with the polarization data which we have not yet resolved. The first is the possibility that different current densities produce different surface roughness factors when dissolving the silver anode. An increased roughness factor would decrease the actual current density and thus the overpotential. The measured electrode potential would then show a relationship to electrode history. We plan to determine the effect of current density on the electrode surface roughness factor.

The second problem is the non-reproducibility of polarization measurements made at current densities below 1 ma/cm^2. This, however, does not severely hinder the comparison of our data with Wagner's theory. A good comparison can be made using the polarization data obtained for the current density range of 1 to 5 ma/cm^2. This fivefold change in current density represents a change in h_a of 13.7 $\frac{mv}{ma/cm^2}$ to 4.3 $\frac{mv}{ma/cm^2}$ or a change of 320% in

k_a/a. (See Figure 1.) The studies of the effect of geometry on current density distribution (Final Report[2] of JPL contract 951554) were also carried out in this current density range.

Possible Use of the Polarization Curve for Surface Area Estimation

Polarization measurements attempted on sintered silver electrodes gave very poor results. The major difficulty was that the potentials drifted indefinitely. A possible explanation for this is that concentration gradients caused by the electrode reaction within the pores of the sintered electrode are very difficult to stir away. This would also account for the poor reproducibility which we experienced.

Because of this problem, we are investigating another system for surface area measurements. The electrode reaction of this system is the evolution of hydrogen at the silver cathode in KOH. There are two advantages to this system. The first is that the electrode surface does not change as the reaction progresses as does the silver anode in ammoniacal electrolyte. The second is that the slope of the polarization curve $d\Delta E/dJ$ is much steeper. Thus much larger errors in the potential measurements can be tolerated.

Conclusions and Future Work

Although some problems were encountered in the polarization measurements, a polarization curve of the silver foil anode in the ammoniacal electrolyte has been obtained which can be used to determine values of h_a for a comparison of our current density distribution data with Wagner's theory. We plan a series of experiments where we will determine J/J_{ave} for various

electrolyte conductivities, σ, electrode widths, $2a$, and current densities (h_a changes as a function of current density). Values of the parameter k_a/a can then be determined from the experimental data and then J/J_{ave} can be calculated from Wagner's theory for comparison.

The ammoniacal-silver anode was found unsatisfactory for surface area determinations of sintered electrodes. An alternate system (H_2 evolution at a silver cathode) is being investigated.

SECTION II

DETERMINATION OF EFFECTIVE

ELECTROLYTIC SURFACE AREA

Introduction

The purpose of our work in this section of the contract is to find and apply methods other than the one previously reported for the determination of the effective electrolytic surface area of sintered silver electrodes[2]. The reason for this is to permit us to check the accuracy of that method, which involves the measurement of the time during which the potential of an $Ag-Ag_2O$ electrode remains essentially constant under the influence of a constant applied current. The principle upon which the method is based is that the thickness of the oxide layer formed on the surface of the silver is a function of the current density. By varying the current applied to an electrode of unknown surface area until the length of the $Ag-Ag_2O$ plateau matches the plateau length of a smooth standard electrode, one can then assume that the electrodes were oxidized at the same current density and have equal depths of penetration. From the current and current density at the unknown electrode, one can calculate the surface area. More detail is given in a previous report[2].

To check this method we have prepared sintered electrodes of calculated known surface area. These were oxidized and their effective electrolytic surface areas were determined.

Experimental

The sintered electrodes of known surface area were prepared from silver powder consisting of spherical silver particles of known diameters. These spherical silver powders were obtained from Particle Information Service, 600 South Springer Road, Los Altos, California 94022. The powders had been separated into various size ranges by an air pressure flow system in which the heavy, large diameter particles were trapped and the light, small diameter particles were collected from the column at different air pressures. The particle size ranges of the powders used in the preparation of the sintered electrodes are given in Table 2. By use of a microscope with a vernier eye piece, the spread of diameters of the particles in a given size range was determined. (Table 3). The distribution is seen to be approximately gaussian.

These powders were pressed into electrodes and sintered at 600°C for 30 minutes. The electrodes were then weighed and the total surface area calculated. The formula used for this calculation is given below.

$$A = \frac{6w}{pd}$$

d = diameter of particle
p = density of silver
w = weight of electrode
A = total surface area

If the surface area is expressed as an area per unit mass (cm^2/gm), the formula is rearranged to give the following:

$$\frac{area}{unit\ mass} = \frac{6}{pd}$$

In this calculation we assume that the total surface area is the sum of the surface areas of the spherical particles that make up the electrode. There is a possible error evident in this assumption. The total surface area will be

less than the sum of the particle surface areas because part of the surface of each of the particles will be pressed against its neighbors. However, if the radius of this contact area is smaller than the depth of penetration of the oxide layer, the quantity of silver oxidized will be virtually unchanged by the contact. Only if the particles are pressed or melted together until the radii of the contact areas become large compared to the depth of penetration does serious error result from the assumption that the entire spherical surface reacts. Microscopic examination of the electrodes shows that little distortion or melting took place. Table 2 lists the calculated surface area per unit mass of sintered electrodes made from particles of each size range. After these electrodes were sintered, they were soaked in 0.1 N KOH for 15 minutes. They were oxidized; the current densities were determined from the standard curve; and the surface area was calculated. The reproducibility of the oxidation runs was ±7%. The effective electrolytic surface areas per unit mass obtained from these experimental measurements are also shown in Table 2.

Results and Discussion

From Table 2, one can see that the percentage error for the smaller size ranges (6 to 9 microns) is much greater than for the large size ranges (24 to 48 microns). Since there is expansion of the silver particles as silver oxide is formed, there is the possibility of a filling of the holes in an electrode if the depth of penetration is sufficient. As the particle size decreases, the dimensions of the open spaces in the electrode also decrease. Therefore, with smaller particles a fixed depth of oxidation is more likely to result in a filling of the open spaces than is the case with larger particles. It appears

probable that entire regions of an electrode prepared from sufficiently small particles can be made electrochemically inactive by being sealed off from the remainder of the electrode.

Calculations made for electrodes prepared from particles of the sizes that we used indicate that the volume increase ranges from about 2% for the largest particles to about 5% for the smallest particles. Since even close packing of spheres gives about 26% open space, it is evident that all holes or pores in the electrodes are not in any case being filled by oxide formation. Therefore, unless very uneven oxidation occurs in our electrodes in the early stages of the run, there appears to be small likelihood of a seal-off of segments of the electrode. Much smaller particles would be required.

Qualitative experiments made upon new vacuum-deposited silver surfaces indicate that 0.1 N KOH does not wet the silver. The discrepancies in surface areas for electrodes with small particles may be caused by non-penetration of electrolyte into the small pores. As noted below, we plan to study this problem.

Future Work

Additional electrodes prepared from spherical particles will be studied in order to resolve the problem of discrepancy of calculated and measured surface areas where small particles are used.

SECTION III

THE EFFECTS OF ULTRASONIC VIBRATIONS

ON THE OXIDATION OF SILVER

Introduction

The depth of oxidation of a smooth silver electrode is a function of the current density. This observation is the basis for a determination of effective electrolytic surface area. In this part of our program, we are determining the extent to which this oxidation depth is altered by physical stresses, such as ultrasonic vibrations.

Skalozubov, Kukoz, and Mikhailenko[4] have observed a 10% increase in charging capacity of sintered silver electrodes by subjecting them to ultrasonic vibrations during the first thirty minutes of the first oxidation. The electrodes were exposed to 21,000 hertz at a power density of 2-3 watts/cm^2 of electrode area at 20 ± 2°C. A mercury-mercuric oxide reference electrode was used to follow the oxidation. Subsequent discharge-charge cycles without vibrations showed that the 10% increase was preserved. Vibrations at 100 hz and an unspecified power density increased the capacity of the sintered electrode up to 20%.

The explanation for this increase in charging capacity was given as an increase in the effective surface area of the silver. Our purpose is to determine whether this increase is caused by (1) fracturing of the oxide layer; (2) increased circulation of electrolyte to previously unreacted silver surfaces; or (3) other factors not yet considered.

Experimental

To eliminate the problems associated with electrolyte circulation through deep pores, silver foil was chosen for initial observations. Silver foil discs with a total geometric surface area of 0.688 cm^2 were oxidized at 150.0 μamps and 20.0 $\pm$ .1°C without the vibrations and the roughness factor was calculated to be 1.16 $\pm$ .02 (Table 4). A mercury-mercuric oxide reference electrode was used to follow the reaction. It was found that the energy and frequency of our ultrasonic generator caused the mercuric oxide to separate from the mercury and remain suspended in the solution. In order to retain confidence in the reference electrode, we used an electrode which could be located outside the ultrasonic vibrator (Figure 2). The silver-silver oxide electrode described by Wales and Burbank[5] was prepared and was found to be suitable. Even with the external reference half-cell, the potential was very unstable during the rise at the end of the plateau (Figure 3). Thermocouples were used to monitor the temperature because thermometers were rendered useless by the vibrations. The temperature of the solution was controlled only to $\pm$2°C because the cooling was not efficient enough to counteract the heating caused by the vibrator. Previous experiments have shown the charging capacity to be very dependent on temperature[2] so the temperature will have to be better controlled.

Data and Results

Oxidations of silver foil subjected to vibrations of a frequency of 80,000 hz and a power density of 120 watts/cm^2 were carried out at 22 $\pm$ 2°C and 218 μamps/cm^2 using the silver-silver oxide reference electrode. The

reproducibility was only ±5% but the roughness factor was 1.25, an increase of 8%. One run was made at a lower current density (98.8 μamps/cm^2) and a roughness factor of 1.45 was obtained for an increase of 25% (Table 4).

Conclusions and Future Work

The increase in charging capacity of a silver foil electrode, caused by ultrasonic vibrations, shows that the increase in effective surface area is probably caused, at least in part, by fracturing of the oxide layer. As one would expect, more fracturing occurs when the oxidation requires a longer time and more fracturing results in a greater increase in charging capacity. The unstable potential during the last stages of oxidation may result as the fractures in the oxide surface intermittently open current paths of reduced resistance. The potential is momentarily depressed until the electrically resistant silver(I) oxide layer covers the fracture.

Future Work

Since depth of oxidation is temperature-dependent, the temperature will be controlled to ±0.1°C. With this refinement, precise measurements of increase in charging capacity at different charging rates will be made. Silver foil will be subjected to the vibrations before oxidation rather than during oxidation to determine the persistence of any strains resulting from the vibrations. Charging capacity will be studied as a function of frequency and power density of the vibrations. Then these experimental techniques will be extended to sintered silver electrodes.

TABLE 1

Extrapolated Polarization Data

Run #	current density (ma/cm^2)	η (extrapolated) (mv)	slope dϕ/dx (mv/inch)	standard deviation (mv)
107	3.22	69.97	809.7	0.4760
110	2.58	59.81	648.3	0.5121
113	1.94	52.78	485.3	0.4190
116	1.61	49.34	405.9	0.4671
119	1.30	45.43	326.0	0.3033
122	0.964	40.53	244.0	0.2136
125	0.645	35.05	162.9	0.3478
128	0.323	28.84	80.60	0.2984
131	2.57	57.64	634.5	0.3831
134	1.93	52.52	476.5	0.2035
137	6.48	81.02	1606.5	0.9987
140	5.78	80.12	1431.5	1.6975
143	5.14	74.83	1273.5	1.1466
146	4.50	72.18	1112.5	0.7992
149	3.86	69.56	953.1	0.6467
152	3.21	64.35	791.7	0.2867
155	1.61	50.89	392.9	0.2521
158	1.28	46.38	315.3	0.4334
161	0.966	42.37	235.6	0.1306
164	0.642	36.48	156.1	0.1715

TABLE 2

Calculated and Experimental Values of the Surface Area per Unit Mass

for Electrodes Prepared from Various Sizes of Spherical Particles

Range of Particle Diameters (microns)	Average Diameter (microns)	Surface area per unit mass (cm^2/mass) calculated	experimental	Discrepancy (%)
6 to 9	7.5	794	457	73
9 to 18	13.5	476	290	64
18 to 36	27	238	200	19
24 to 48	36	178	171	4

TABLE 3

Particle Counts of Spherical Silver Particles

24 to 48 micron range		6 to 9 micron range	
number of particles	diameter size in microns	number of particles	diameter size in microns
3	46	1	10
16	39	8	9
17	33	22	8
11	26	18	7
2	20	1	6
particles 50	average 33	particles 50	average 8

TABLE 4

Effect of Ultrasonic Vibrations Upon

the Roughness Factor of Silver Foil

| Current (μamps)	Temperature (°C.)	Plateau Length (Minutes)	Ultrasonic Vibrations	Roughness Factor
150.0	20.0 ± 0.1	4.70	No	1.18
150.0	20.0 ± 0.1	4.75	No	1.18
150.0	20.0 ± 0.1	4.45	No	1.14
150.0	20.0 ± 0.1	4.30	No	1.12
150.0	20.0 ± 0.1	4.10	No	1.08
150.0	20.0 ± 0.1	4.95	No	1.21
150.0	20.0 ± 0.1	4.75	No	1.18
150.0	20.0 ± 0.1	4.80	No	1.19
150.0	20.0 ± 0.1	4.50	No	1.15
150.0	20.0 ± 0.1	4.47	No	1.14
150.0	22 ± 2	5.30	Yes	1.26
150.0	22 ± 2	5.55	Yes	1.28
150.0	22 ± 2	5.60	Yes	1.29
150.0	22 ± 2	4.80	Yes	1.19
150.0	22 ± 2	4.90	Yes	1.20
68.0	22 ± 2	17.30	Yes	1.45
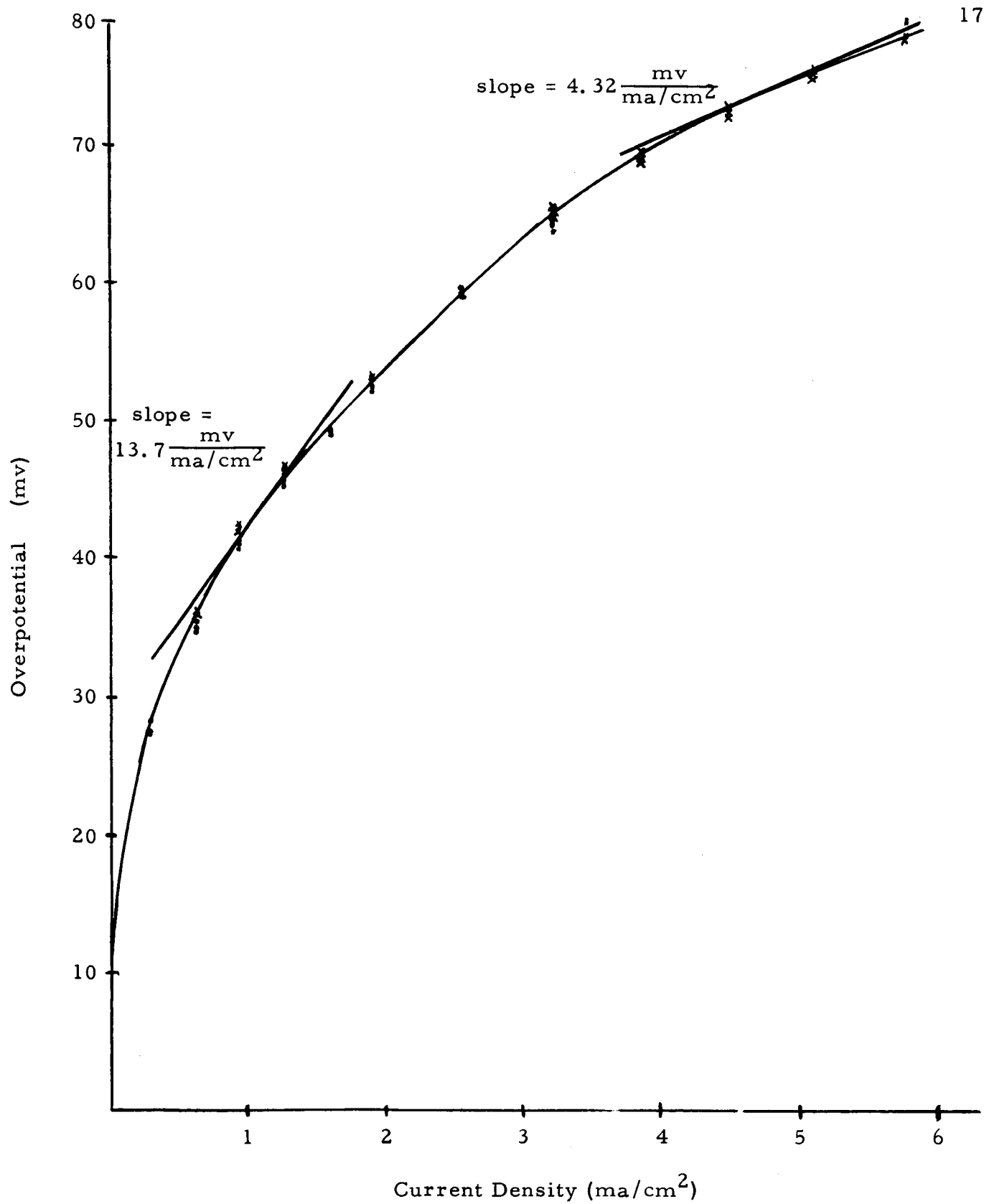
Figure 1   Polarization curve for the ammoniacal silver foil electrode.
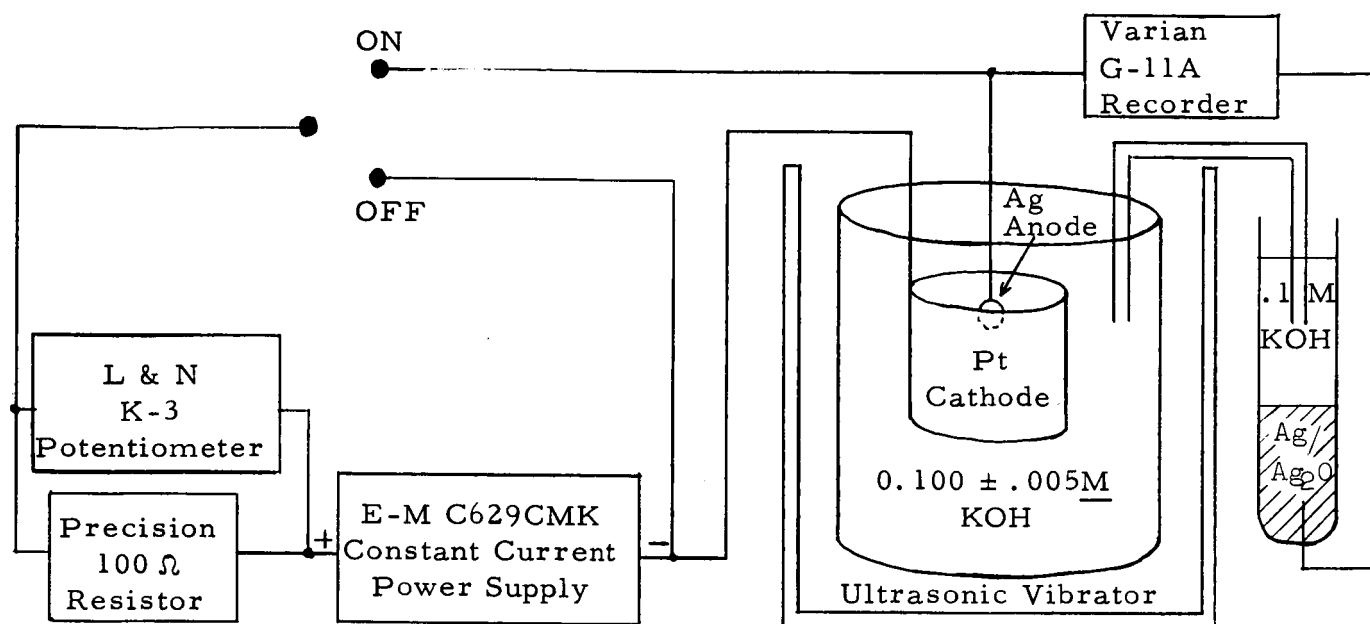
Figure 2   Apparatus used to oxidize silver foil in an ultrasonic vibrator.

Time (minutes)

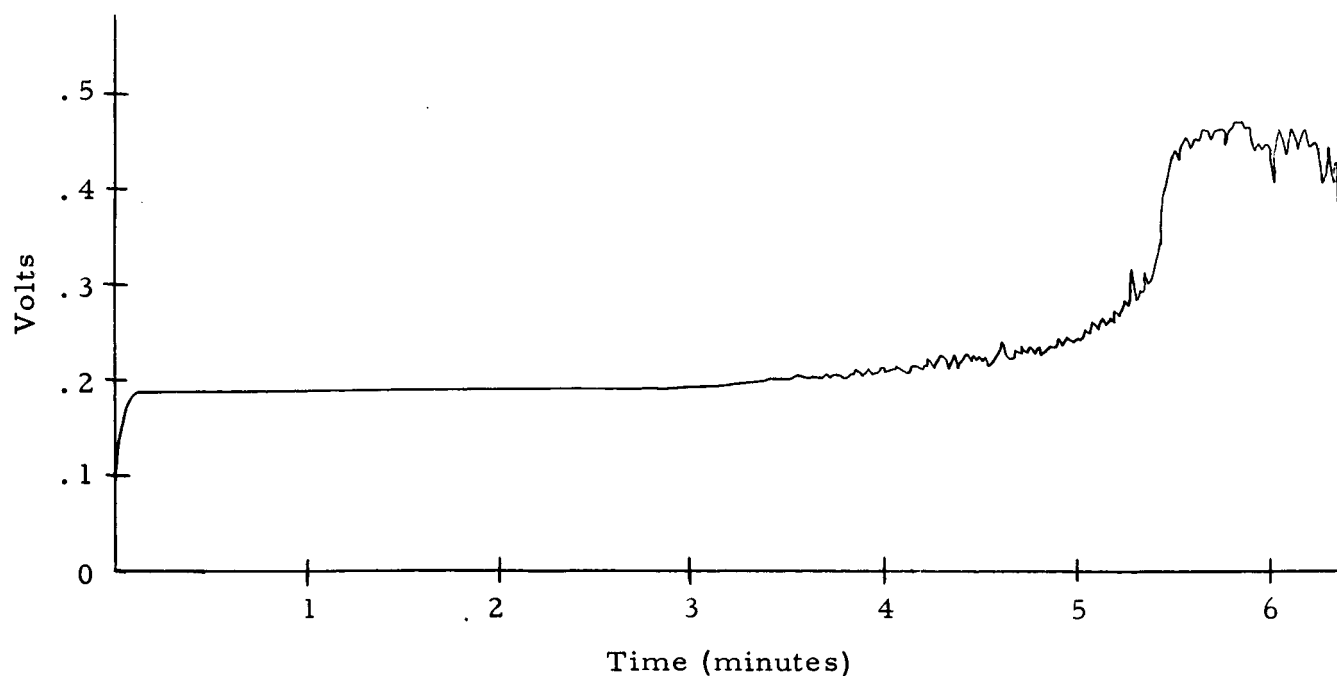Figure 3   A potential vs. time curve for the first oxidation plateau of silver subjected to ultrasonic vibrations.

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